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MANUFACTURING METHOD FOR PHOTOVOLTAIC DEVICE  
[Hikarikidenryokusoshi no seizouhouhou]

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## 1. Title of the Invention

MANUFACTURING METHOD FOR PHOTOVOLTAIC DEVICE

## 2. Claim

(1) A manufacturing method for photovoltaic devices characterized by forming a first amorphous semiconductor layer that consists of amorphous silicon germanium or amorphous germanium and forming an amorphous silicon layer in that order on a substrate, by then subjecting them to a heat treatment in order to crystallize each of said amorphous layers, and by thus forming a first polycrystalline semiconductor layer, which consists of polycrystalline silicon germanium or polycrystalline germanium, and a polycrystalline silicon layer.

## 3. Detailed Explanation of the Invention

(Field of Industrial Application)

The present invention pertains to manufacturing methods for photovoltaic devices that are utilized as solar cells, photosensors, etc.

(Related Art)

In general, a photovoltaic device has a structure in which the following are layered in that order on a transparent substrate, such as glass: a transparent electrode; 3 layers of amorphous semiconductor layers of p, i (intrinsic), and n conductivity types; and a rear-surface electrode.

Such a photovoltaic device has an advantage in that it is inexpensive but has a problem in that the photoelectric conversion efficiency is low in comparison to a photovoltaic device in which crystalline silicon is

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\* Numbers in the margin indicate pagination in the foreign text.

utilized.

Moreover, the photosensitivity range of a photovoltaic device in which amorphous semiconductor layers are utilized is 300~900nm, but there has been an increasing need for photovoltaic devices that are sensitive to wavelengths longer than that.

For this reason, photovoltaic devices in which polycrystalline silicon is utilized are attracting attention. Compared to amorphous silicon, polycrystalline silicon has characteristics in that its mobility is higher by about 1~2 figures, is thermally stable, and is highly reliable. Moreover, its photosensitivity range is 300~1200nm and wide.

Conventionally, polycrystalline silicon is formed by means of so-called solid-phase growth, in which amorphous silicon is formed on a substrate usually by means of a CVD technique to reduce the cost and in which this substrate is subjected to a heat treatment inside a vacuum container in order to crystallize the amorphous silicon layer.

[Problems that the Invention is to Solve]

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The above-described conventional method has a problem in that the solid-phase growth temperature has to be 500°C or higher in order to directly form polycrystalline silicon on the substrate and in that it is difficult to utilize glass, which is inexpensive, as the substrate.

Moreover, since only polycrystalline silicon has been formed in the past, it was impossible to form a multibandgap photovoltaic device. Multibandgap solar cells are divided into devices that consist of 2 or more p/n or pin junctions. However, there are problems in that the characteristics of a device in which germanium (Ge) or silicon germanium

(SiGe) is utilized for the power generation layer are poor and in that currents cannot be extracted effectively from light of a long wavelength.

The present invention was completed in light of such situation, and it supplies a method for manufacturing multibandgap photovoltaic devices as well as reduces the temperature of the solid-phase growth.

#### [Means for Solving the Problems]

The present invention is characterized by forming a first amorphous semiconductor layer that consists of amorphous silicon germanium or amorphous germanium and forming an amorphous silicon layer in that order on a substrate, by then subjecting them to a heat treatment in order to crystallize each of said amorphous layers, and by thus forming a first polycrystalline semiconductor layer, which consists of polycrystalline silicon germanium or polycrystalline germanium, and a polycrystalline silicon layer.

#### [Operation of the Invention]

Amorphous silicon germanium (a-SiGe) or amorphous germanium (a-Ge) grows in a solid phase at a low temperature of 400°C. Therefore, the solid-phase growth of a-SiGe or a-Ge is started by a 400°C heat treatment, and this advances to the growth of amorphous silicon (a-Si) layer and a-Si from solid phase. In a single body of a-Si, solid-phase growth of a-Si is allowed to take place at 400°C, at which temperature solid-phase growth does not occur.

Furthermore, since a substrate, a semiconductor layer that consists of polycrystalline silicon germanium or polycrystalline germanium, and a polycrystalline silicon layer can be formed in this order, a multibandgap

photovoltaic device can be formed.

Moreover, extraction of currents from the germanium or silicon germanium layer, from which current conventionally could not be extracted effectively, can be carried out effectively.

Figure 1, (a) and (b), are cross-sectional drawings showing the manufacturing method for a photovoltaic device of the present invention. Figure 1(a) shows a state before the heat treatment and Fig. 1(b) shows a state after a heat treatment.

As shown in Fig. 1(a), the first amorphous semiconductor layer [2] consisting of a-SiGe or a-Ge is formed on a substrate [1] that is made of quartz, etc.

The above-described first amorphous semiconductor layer [2] is formed on the substrate [1] by a plasma CVD technique. If an a-SiGe layer is formed as the first amorphous semiconductor layer [2],  $\text{SiH}_4$  and  $\text{GeH}_4$  are utilized as the material gases, and if an a-Ge layer is formed,  $\text{GeH}_4$  is utilized as the material gas. Moreover, the ratio of Si and Ge inside the a-SiGe layer can be flexibly changed by altering the gas flow ratio of  $\text{SiH}_4$  and  $\text{GeH}_4$ .

On this first amorphous semiconductor layer [2], the amorphous silicon layer [3] is formed also by the plasma CVD technique. The material gas utilized for the formation of this amorphous silicon layer [3] is  $\text{SiH}_4$ .

Then, an amorphous-type device obtained by sequentially forming the first amorphous silicon layer [2] and the amorphous silicon layer [3] on the substrate [1] as described earlier is placed inside a vacuum

container and is subjected to a heat treatment for about 10 hours while the temperature is kept at 400°C.

Through this heat treatment, the amorphous semiconductor layer is crystallized, and so-called solid-phase growth in which a first polycrystalline semiconductor layer [21], which consists of polycrystalline silicon germanium or polycrystalline germanium, and a polycrystalline silicon layer [31] are formed takes place as shown in Fig. 1(b).

At this time, although solid-phase growth does not occur in a-Si by itself at 400°C, a-SiGe or a-Ge grows in a solid phase at 400°C. Therefore, solid-phase growth advances through the a-Si layer [3]. In this manner, a-SiGe or a-Ge promotes the solid-phase growth of a-Si.

Moreover, the solid-phase growth temperature is related to the /373 amount of Ge, and the larger the amount of Ge, the lower the temperature of the solid-phase growth can be made. Figure 2 shows the relationship between the amount of Ge and the temperature that can cause solid-phase growth. As is clear from Fig. 2, the temperature of solid-phase growth becomes lower along with the amount of Ge. Therefore, the solid-phase growth temperature can be made the lowest when the starting material is a substrate/a-Ge/a-Si.

In this manner, by using a substrate [1] that has layered on it a first amorphous semiconductor layer [2] consisting of a-SiGe or a-Ge and an a-Si layer [3] in that order as the starting material, the temperature for solid-phase growth can be lowered, and at the same time, a multibandgap photovoltaic material, in which semiconductors with different band gaps

are layered, can be formed.

Moreover, the band gap of a semiconductor layer [21], which consists of polycrystalline silicon germanium or polycrystalline germanium, is 0.9~1.1eV, and the band gap of a polycrystalline silicon layer is 1.1~1.3eV.

Figure 3 is a structural drawing of a photovoltaic device obtained by using said multibandgap photovoltaic material. In the structure of the device, an n-type polycrystalline Ge [41], a polycrystalline SiGe or polycrystalline Ge layer [42], a polycrystalline Si layer [4], and a p-type polycrystalline Si layer [44] are sequentially formed.

Figures 4(a) through 4 (f) are cross-sectional drawings showing each process of a manufacturing example of the photovoltaic device illustrated in Fig. 3. The above manufacturing method for the photovoltaic device will be explained based on Fig. 4.

First, an n-type a-Ge layer [4] is formed on a quartz substrate [1] by a plasma CVD technique and is then subjected to solid-phase growth as shown in Fig. 4(a). Then, an n-type polycrystalline Ge layer [41] is formed on a quartz substrate [1] as shown in Figure 4(b). This n-type polycrystalline Ge layer [41] has a sheet resistance of  $\sim 10\Omega/\square$  and acts also as an electrode.

Next, as shown in Fig. 4(c), an amorphous semiconductor layer [5] that consists of a-SiGe or a-Ge and an a-Si layer [6] are formed in layers by the plasma CVD technique. Then, as shown in Fig. 4(d), a multibandgap photovoltaic material that is made up of a polycrystalline semiconductor layer [42], which consists of polycrystalline SiGe or polycrystalline



Ge, and of a polycrystalline Si layer [43] is formed.

Next, a p-type a-Si layer [7] is formed by the plasma CVD technique as shown in Fig. 4(e), and a p-type polycrystalline Si layer [44] is formed by the solid-phase growth technique as shown in Fig. 4(f). This p-type polycrystalline Si layer [44] has a sheet resistance of  $\sim 10\Omega/\square$ .

Figure 5 indicates the collection efficiency of a photovoltaic device of this invention [A] in which a multibandgap photovoltaic material is utilized. For comparison, the collection efficiency of a polycrystalline Si (single-crystal silicon) photovoltaic device [B] is indicated. The collection efficiency of the photovoltaic device [A] of this invention in which a multibandgap photovoltaic material is utilized is higher than the collection efficiency of the c-Si photovoltaic device [B] in the long-wavelength range of 1000nm or more, and its sensitivity reaches up to 1300nm. In this manner, the multibandgap photovoltaic material is also excellent as a material for solar cells.

#### [Effects of the Invention]

As explained earlier, solid-phase growth of amorphous silicon germanium or amorphous germanium starts at a low temperature. This growth advances through the amorphous silicon layer, causing the solid-phase growth of a-Si to take place. The solid-phase growth of the amorphous silicon takes place at a low temperature at which the solid-phase growth of a-Si alone does not take place, and therefore, the temperature of solid-phase growth can be lowered.

Furthermore, since a substrate, a polycrystalline semiconductor layer, which consists of polycrystalline silicon germanium or

polycrystalline germanium, and a polycrystalline silicon can be formed in that order, it is possible to form a multibandgap photovoltaic device.

#### 4. Brief Explanation of the Drawings

Figure 1, (a) and (b), are cross-sectional drawings that show the manufacturing method of a photovoltaic device of the present invention.

Figure 2 is a graph that shows the relationship between the temperatures at which solid-phase growth can occur and the amounts of Ge.

Figure 3 is a cross-sectional drawing showing a multibandgap photovoltaic device for which the present invention is utilized.

Figure 4, (a) through (f), are cross-sectional drawings showing each process of the manufacturing method of the photovoltaic device shown in Fig. 3.

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Figure 5 is a characteristics graph indicating the collection efficiencies of a photovoltaic device of this invention and of a conventional photovoltaic device.

[1] = substrate

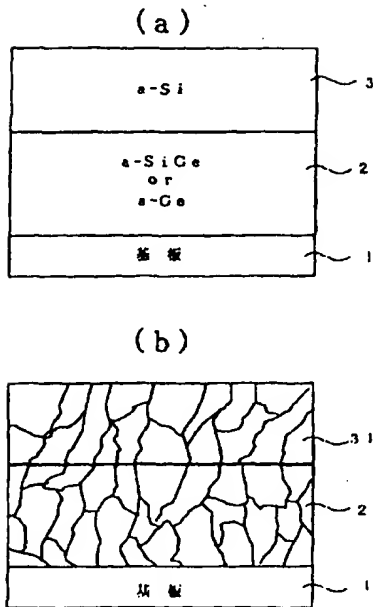
[2] = first amorphous semiconductor layer

[3] = amorphous silicon layer

[21] = first polycrystalline semiconductor layer

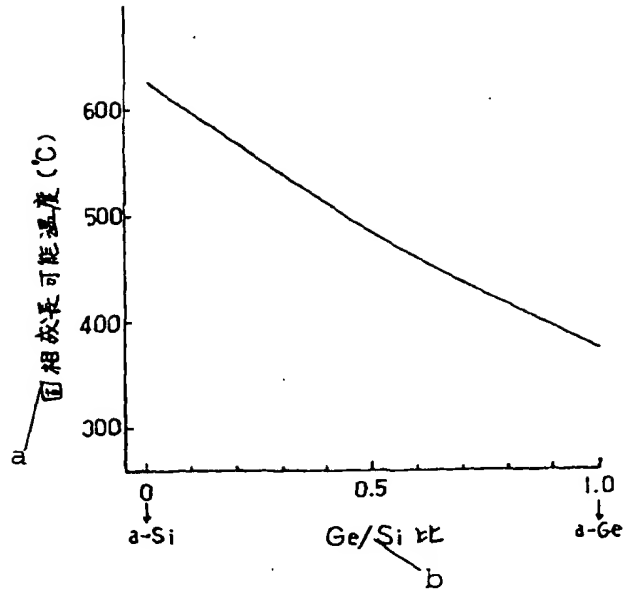
[31] = polycrystalline silicon layer

Figure 1



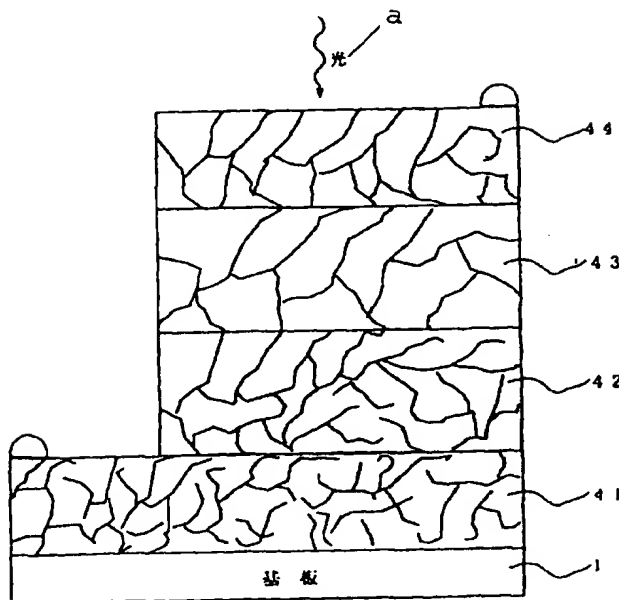
Key: 1) substrate.

Figure 2



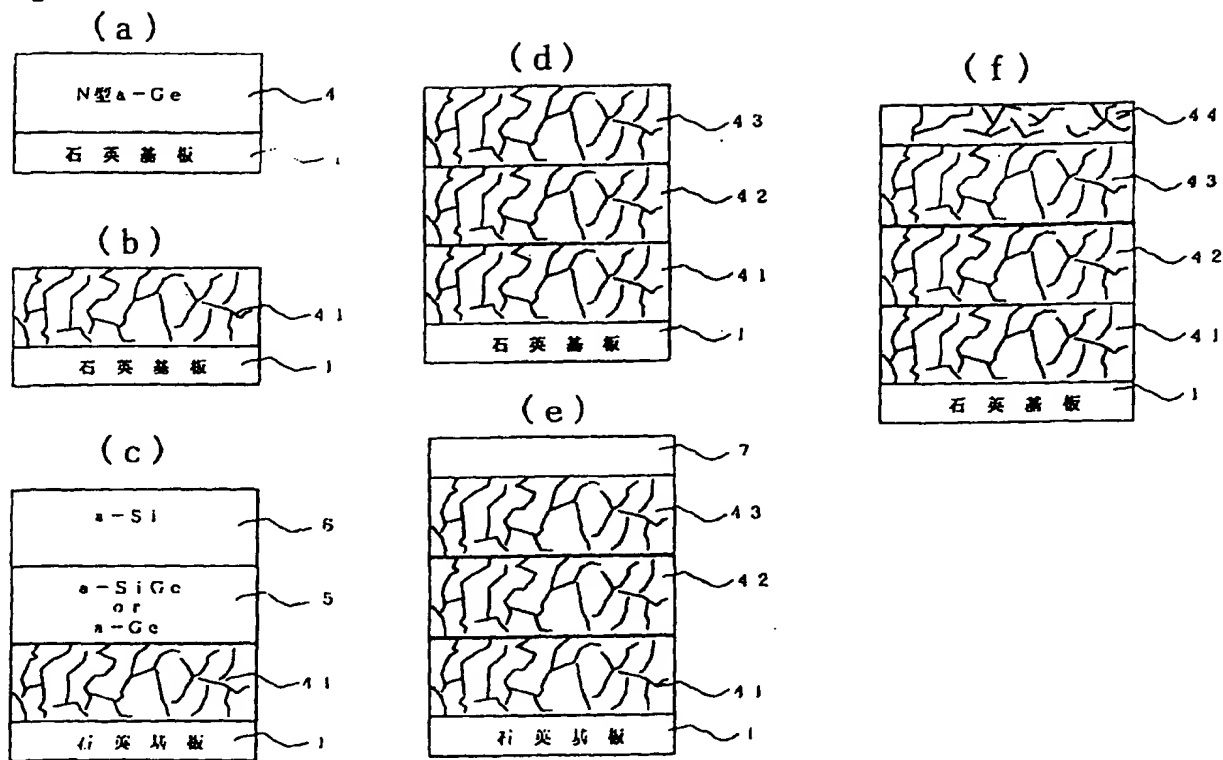
Key: a) Temperatures (°C) at which solid-phase growth can occur; b) Ge/Si Ratio.

Figure 3



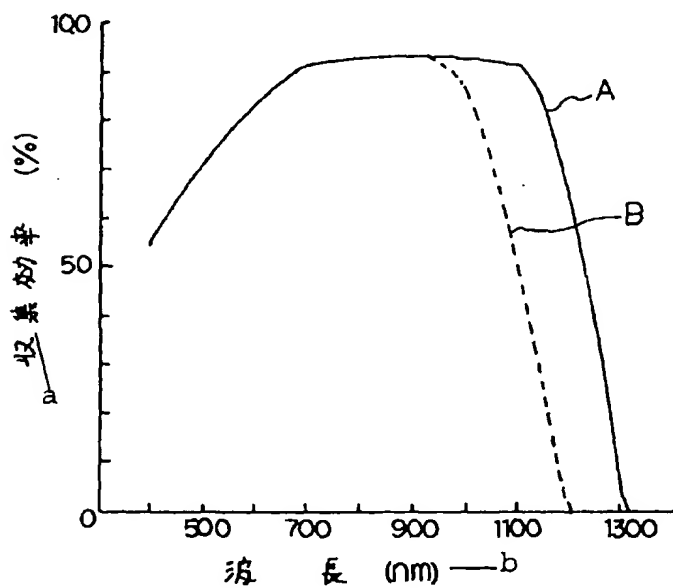
Key: 1) substrate; a) light.

Figure 4



Key: 1) quartz substrate; 4) N-type a-Ge.

Figure 5



Key: a) Collection Efficiency (%); b) Wavelength (nm).